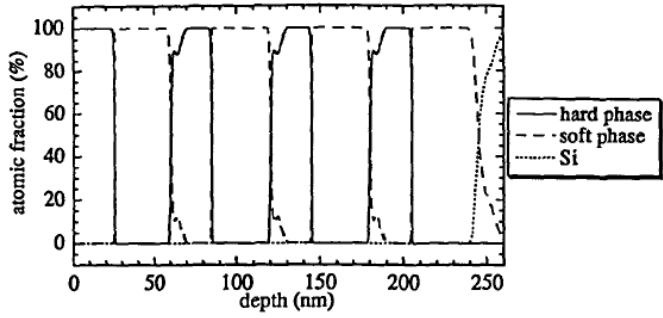
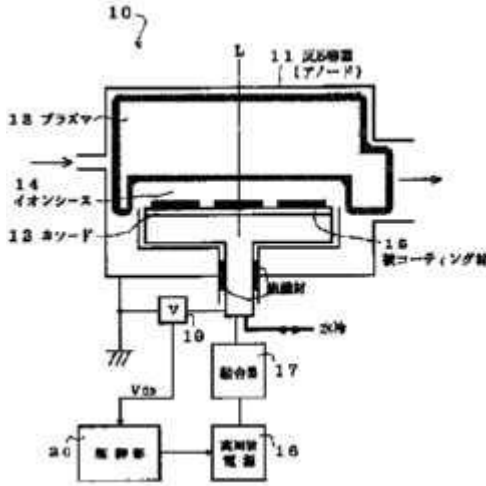


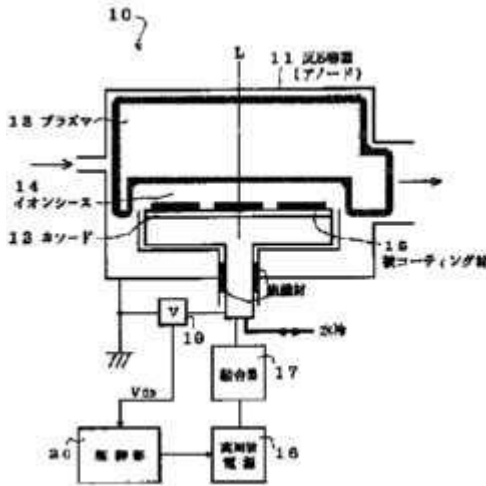
**EXHIBIT B****§ 102 REFERENCES COVERING CLAIMS**

<b>'399 Patent</b>	<b>"Mechanical Properties of Amorphous Hard Carbon Films Prepared by Cathodic Arc Deposition," Simone Anders, Andre Anders, Joel W. Ager, Zhi Wang, George M. Pharr, Ting Y. Tsui, Ian G. Brown and C. Singh Bhatia; Materials Research Society Symposium Proceedings, Volume 383 ("Anders-MRSSP")</b>
<b><u>Claim 1</u></b>	
A hard carbon thin film arrangement comprising	The Anders-MRSSP reference was published in 1995. This is greater than one year before the '399 patent's priority date of Mar. 19, 1997.
a hard carbon thin film having a surface and	In the present paper we report on mechanical properties of cathodic-arc deposited hard carbon films which were formed at various bias voltages. In particular, we have formed multilayers of alternating hard and soft amorphous carbon films by varying the bias voltage during deposition. "Soft" in this case means films with hardness in the range of 15-25 GPa [6] which is much smaller than the maximum hardness of 60 GPa [12] that can be obtained for films deposited by this method but is still very hard in comparison to other thin films. The multilayers have been investigated by transmission electron microscopy and nanoindentation. Stress measurements have been performed also. (Anders-MRSSP at 453).
an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and	Three different multilayer structures have been deposited. All three structures consisted of 8 layers; the first layer at the substrate interface was a soft layer deposited at - 2 kV pulsed bias, and the top layer was a hard layer deposited at - 100 V pulsed bias. The ratio between the amount of carbon deposited at high and low bias was varied for the three structures. For the first structure the ratio was 50% soft phase/50% hard phase, for the second structure it was 10% soft phase/90% hard phase, and for the third structure it was 90% soft phase/10% hard phase. The total thickness of the multilayer structures was 250 nm. For comparison, films were deposited at high bias and low bias voltage only with the same total film thickness of 250 nm. Fig. 1 shows a simulation of the deposition for the 50% soft phase/50% hard

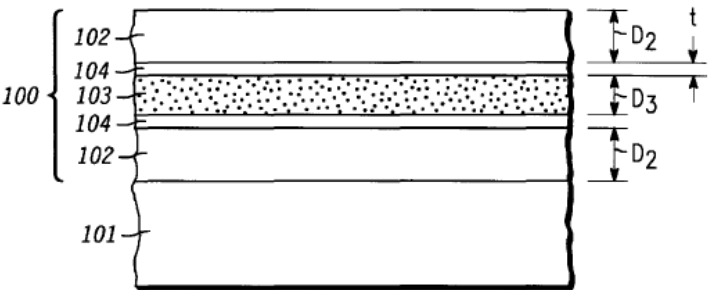
'399 Patent	<p><b>“Mechanical Properties of Amorphous Hard Carbon Films Prepared by Cathodic Arc Deposition,” Simone Anders, Andre Anders, Joel W. Ager, Zhi Wang, George M. Pharr, Ting Y. Tsui, Ian G. Brown and C. Singh Bhatia; Materials Research Society Symposium Proceedings, Volume 383 (“Anders-MRSSP”)</b></p>
	<p>phase structure using the code T-DYN 4.0 [13].</p>  <p>Fig. 1: Simulation of multilayer deposition for 50% soft phase/50% hard phase structure using the code T-DYN 4.0 (Anders-MRSSP at 454).</p>
<p>having a graded carbon composition in which a ratio of <math>sp^2</math> to <math>sp^3</math> carbon-carbon bonding in said thin film decreases in said thickness direction from said interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<p>Since the mass density of the soft (<math>2.15 \text{ g/cm}^3</math>) and hard (<math>3.0 \text{ g/cm}^3</math>) phases are different, the layer thickness is 25 nm for the hard phase and 35 nm for the soft phase. The soft phase shows a considerable intermixing with the underlying layers (Si or hard phase carbon) due to the high energy of the ions during the deposition whereas the hard phase shows only very small intermixing because the ion energy is low. (Anders-MRSSP at 454).</p> <p>The difference in the thickness of the soft and hard layers is due to the different densities of the layers. Measurements of the mass density of soft and hard single layers determined by electron energy loss spectroscopy (EELS) [12] and by Rutherford backscattering spectroscopy and profilometry [6] result in densities of <math>2.1\text{-}2.2 \text{ g/cm}^3</math> and <math>2.8\text{-}3.0 \text{ g/cm}^3</math>, respectively. This large difference is probably the reason for the difference in the contrast of soft and hard layers in the TEM image. The simulation (Fig. 1) predicts a ratio between the thickness of the soft to the hard layer of 1.4 based on the ratio of the densities. The TEM picture shows a ratio of almost 2; this might be due to the additional effect of intermixing and possible softening of the hard layers by ion bombardment during deposition of the following soft layer. This is supported by the fact that the top hard layer is thicker</p>

<b>'399 Patent</b>	<b>“Mechanical Properties of Amorphous Hard Carbon Films Prepared by Cathodic Arc Deposition,” Simone Anders, Andre Anders, Joel W. Ager, Zhi Wang, George M. Pharr, Ting Y. Tsui, Ian G. Brown and C. Singh Bhatia; Materials Research Society Symposium Proceedings, Volume 383 (“Anders-MRSSP”)</b>
	<p>than all other hard layers inside the structure. (Anders-MRSSP at 456).</p> <p>The mechanical properties of the multilayers such as hardness and elastic modulus were found to be a linear interpolation between the properties of single layers of the same thickness as the multilayer structure. This might not be the case for all multilayer structures; it is possible that the hardness can even be increased by forming multilayers [16-18] with a larger number of layers than has been investigated in this paper. It is very interesting to note that in contrast to hardness and elastic modulus the stress is not a linear interpolation between single layer properties but is considerably lower. It can be expected that the stress can be further reduced by reducing the layer thickness and increasing the number of layers in the structure. This gives the opportunity of changing to a certain degree independently the hardness and stress in the structure. It has been reported for hydrogen-free and hydrogenated amorphous carbon films [1, 5, 19, 20] that hardness (fraction of <math>sp^3</math> bonds) and stress are directly correlated. and models have been developed describing the formation of <math>sp^3</math> bonds as stress-induced [21]. The stress in very hard amorphous carbon films can reach high values, larger than 10 GPa [II]. Reducing the stress and containing the hardness at the same time was possible only by introducing additional chemical elements in the films as has been described for nitrogen incorporation [22]. The formation of multilayers offers an interesting alternative. It is also possible to deposit amorphous hard carbon films with a gradually varying bias voltage and to tailor in this way the film properties throughout the film the during the growth. (Anders-MRSSP at 457).</p>

'399 Patent	<p><b>“Method For Production Of Diamond-Like Carbon Thick Film And Apparatus Therefor,” Tsuji Osamu, Patent Abstracts of Japan, 1994; JP06-033239A (“Japan – 06-33239”)</b></p>
<p><b><u>Claim 1</u></b></p>	
<p>A hard carbon thin film arrangement comprising</p>	<p>The Japan – 06-33239 reference was published in Feb. 8, 1994. This is greater than one year before the '399 patent's priority date of Mar. 19, 1997.</p>
<p>a hard carbon thin film having a surface and</p>	<p>PURPOSE: To form thick diamond-like carbon(DLC) films which do not peel by changing the high-frequency electric power to be impressed to a cathode at the time of forming the DLC films on substrates by cracking of gaseous hydrocarbon in a cathode coupling type plasma reactor.</p> <p>CONSTITUTION: The gaseous hydrocarbon is introduced into a reactor 11 as the anode of the cathode coupling type plasma reactor 10. The high-frequency voltage is then applied from a power source 18 via a coupler 17 to the cathode 12 placed with the substrates 15. The gaseous hydrocarbon is converted to plasma and cracked by a glow discharge, by which the amorphous diamond-like carbon films having high hardness are formed on the substrates 15. The high-frequency electric power impressed to the cathode 12 is changed by a control section 20 in such a manner that the self-bias voltage <math>V_{dc}</math> in an ion sheath 14 formed near the cathode 12 increases or decreases with time. The DLC films which do not peel and crack even if the films are as thick as about 20 to 30<math>\mu</math>m are formed on the surface of the substrates 15.</p> <p>(Japan 06-33239 at Abstract).</p>  <p>(Japan 06-33239 at Abstract).</p>

'399 Patent	<p><b>“Method For Production Of Diamond-Like Carbon Thick Film And Apparatus Therefor,” Tsuji Osamu, Patent Abstracts of Japan, 1994; JP06-033239A (“Japan – 06-33239”)</b></p>
<p>an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and</p>	<p>PURPOSE: To form thick diamond-like carbon(DLC) films which do not peel by changing the high-frequency electric power to be impressed to a cathode at the time of forming the DLC films on substrates by cracking of gaseous hydrocarbon in a cathode coupling type plasma reactor.</p> <p>CONSTITUTION: The gaseous hydrocarbon is introduced into a reactor 11 as the anode of the cathode coupling type plasma reactor 10. The high-frequency voltage is then applied from a power source 18 via a coupler 17 to the cathode 12 placed with the substrates 15. The gaseous hydrocarbon is converted to plasma and cracked by a glow discharge, by which the amorphous diamond-like carbon films having high hardness are formed on the substrates 15. The high-frequency electric power impressed to the cathode 12 is changed by a control section 20 in such a manner that the self-bias voltage <math>V_{dc}</math> in an ion sheath 14 formed near the cathode 12 increases or decreases with time. The DLC films which do not peel and crack even if the films are as thick as about 20 to 30<math>\mu</math>m are formed on the surface of the substrates 15.</p> <p>(Japan 06-33239 at Abstract).</p>  <p>(Japan 06-33239 at Abstract).</p>
<p>having a graded carbon composition in which a ratio of <math>sp^2</math> to <math>sp^3</math> carbon-carbon bonding in said thin film decreases in said thickness direction from said</p>	<p>“Besides the purpose of the above exfoliations and crack prevention, by making the auto-bias voltage <math>V_{dc}</math> fluctuate arbitrarily between DLC membrane making processes, the compression stress and hardness in the DLC membrane can be changes to a thickness direction, and various slope</p>

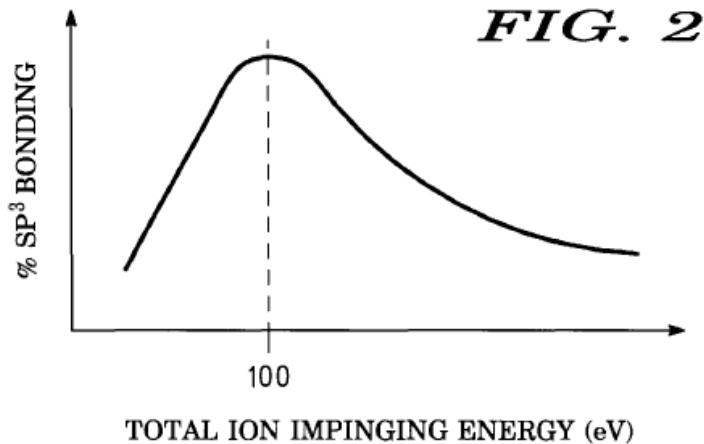
<b>'399 Patent</b>	<b>“Method For Production Of Diamond-Like Carbon Thick Film And Apparatus Therefor,” Tsuji Osamu, Patent Abstracts of Japan, 1994; JP06-033239A (“Japan – 06-33239”)</b>
interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.	characteristics can be given. Thereby, the DLC membrane according to the various purposes can be arbitrarily produced now.” (Japan – 06-33239 at [0014] (machine translation))

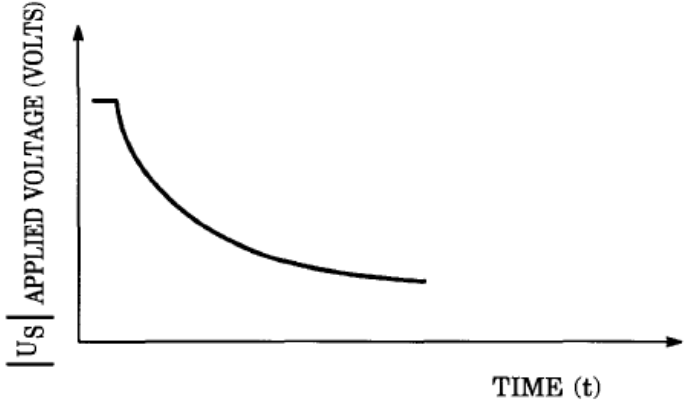
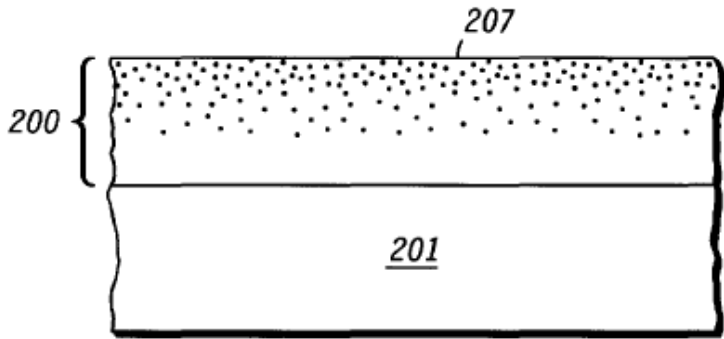
'399 Patent	U.S. Patent No. 5,837,331 ("331 Patent")
<u>Claim 1</u>	
A hard carbon thin film arrangement comprising	The '331 Patent reference was filed on Mar. 13, 1996. This is prior to the '399 patent's priority date of Mar. 19, 1997.
a hard carbon thin film having a surface and	 <p data-bbox="735 766 920 804"><b>FIG. 1</b></p> <p data-bbox="646 808 932 842">('331 patent at Fig. 1).</p> <p data-bbox="646 877 1422 1900">Referring now to FIG. 1 there is depicted a cross-elevational view of an amorphous multi-layered structure <b>100</b>, which is realized by performing various steps of a method in accordance with the present invention. Amorphous multi-layered structure <b>100</b> is formed on a deposition substrate <b>101</b> and includes a pair of first-phase layers <b>102</b> and a second-phase layer <b>103</b>. Deposition substrate <b>101</b> is made from glass or silicon. In this particular embodiment, pair of first-phase layers <b>102</b> have the same physical, electrical, and chemical properties, while second-phase layer <b>103</b> has physical, electrical, and/or chemical properties which are distinct from those of first-phase layers <b>102</b>. In other embodiments of a method in accordance with the present invention, multi-layer structures are realized in which each of the constituent layers has a distinct set of properties; alternatively, other structures can be realized which include many layers having alternating properties so that the structures have a periodicity which can be modulated. Located between each first-phase layer <b>102</b> and second-phase layer <b>103</b> is a transition layer <b>104</b>. First-phase layers <b>102</b> have equal thicknesses, <math>D_2</math>, which are distinct from the thickness, <math>D_3</math>, of second-phase layer <b>103</b>. In general, in order to exhibit quantum size effects (quantum wells, coupled quantum wells, superlattices, tunneling, etc.), thicknesses <math>D_2</math> and <math>D_3</math> are within the range of 0-100 angstroms, and the thickness, <math>t</math>, of transition layer <b>104</b> is less than one atomic layer. In accordance with the method of the present invention, first-phase layers <b>102</b> and second-phase</p>

'399 Patent	U.S. Patent No. 5,837,331 ("331 Patent")
	<p>layer <b>103</b> are made from a precursor of a multi-phase material. That is, the original material is the same. A multi-phase material is a solid material which can exist in different phases or micro structures, the relative compositions of which determine the properties of a given structure comprised of the multi-phase material. To aid understanding, and as will be described in greater detail below, the distinctive properties of first-phase layers <b>102</b> and second-phase layer <b>103</b> are attributable to the difference in the energy of the formative ions as they impinge upon the growing solid layer. This impinging energy of the ions is a significant factor in determining the types, and relative amounts, of chemical bonds formed during the deposition of first-phase layers <b>102</b> and second-phase layer <b>103</b>. ('331 patent at 3:6-47).</p>
<p>an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and</p>	<div data-bbox="649 835 1360 1129" data-label="Image"> </div> <p><b>FIG. 1</b> (‘331 patent at Fig. 1).</p> <p>Referring now to FIG. 1 there is depicted a cross-elevational view of an amorphous multi-layered structure <b>100</b>, which is realized by performing various steps of a method in accordance with the present invention. Amorphous multi-layered structure <b>100</b> is formed on a deposition substrate <b>101</b> and includes a pair of first-phase layers <b>102</b> and a second-phase layer <b>103</b>. Deposition substrate <b>101</b> is made from glass or silicon. In this particular embodiment, pair of first-phase layers <b>102</b> have the same physical, electrical, and chemical properties, while second-phase layer <b>103</b> has physical, electrical, and/or chemical properties which are distinct from those of first-phase layers <b>102</b>. In other embodiments of a method in accordance with the present invention, multi-layer structures are realized in which each of the constituent layers has a distinct set of properties; alternatively, other structures can be realized which include many layers having alternating properties so that the</p>



'399 Patent	U.S. Patent No. 5,837,331 ("331 Patent")
	<p>structures have a periodicity which can be modulated. Located between each first-phase layer <b>102</b> and second-phase layer <b>103</b> is a transition layer 104. First-phase layers <b>102</b> have equal thicknesses, D2, which are distinct from the thickness, D3, of second-phase layer 103. In general, in order to exhibit quantum size effects (quantum wells, coupled quantum wells, superlattices, tunneling, etc.), thicknesses D2 and D3 are within the range of 0-100 angstroms, and the thickness, t, of transition layer <b>104</b> is less than one atomic layer. In accordance with the method of the present invention, first-phase layers <b>102</b> and second-phase layer <b>103</b> are made from a precursor of a multi-phase material. That is, the original material is the same. A multi-phase material is a solid material which can exist in different phases or micro structures, the relative compositions of which determine the properties of a given structure comprised of the multi-phase material. To aid understanding, and as will be described in greater detail below, the distinctive properties of first-phase layers <b>102</b> and second-phase layer <b>103</b> are attributable to the difference in the energy of the formative ions as they impinge upon the growing solid layer. This impinging energy of the ions is a significant factor in determining the types, and relative amounts, of chemical bonds formed during the deposition of first-phase layers <b>102</b> and second-phase layer 103. ('331 patent at 3:6-47).</p>
<p>having a graded carbon composition in which a ratio of <math>sp^2</math> to <math>sp^3</math> carbon-carbon bonding in said thin film decreases in said thickness direction from said interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<p>The deposited structures are amorphous, which includes structures having no long-range order and composite structures that have inclusions of nano-sized clusters disposed within a matrix having no long-range order. For example, in a method for forming an amorphous multi-layered structure in accordance with the present invention the precursor of a multi-phased material is graphite, which is vaporized to form carbon ions. When deposited on deposition substrate 101, the carbon ions impinge upon the solid to form a solid layer having relative compositions of <math>sp^3</math>-bonded carbon atoms and <math>sp^2</math>-bonded carbon atoms. The relative compositions of <math>sp^3</math>-bonded carbon atoms and <math>sp^2</math>-bonded carbon atoms are determinative of certain properties of the solid, amorphous carbon layer. These properties include resistivity, electronic emission, band gap, density, hardness, and stress. For example, a layer of carbon having a high relative composition of <math>sp^2</math>-bonded carbon atoms has a low resistivity, whereas a layer of carbon having</p>

'399 Patent	U.S. Patent No. 5,837,331 ("331 Patent")
	<p>a high relative composition of <math>sp^3</math>-bonded carbon atoms has a high resistivity. If a certain property value is desired for a given layer, such as the value of the band gap, and if the relationship between relative composition, or <math>\%sp^3</math>, and this particular property is known, the relative composition can be specified. Then, if the relationship between the relative composition and total ion impinging energy, E, is known, a total ion impinging energy can be specified to realize the desired value of the given property. (‘331 patent at 3:59-4:19).</p> <div data-bbox="657 682 1356 1123"> <p style="text-align: right;"><b>FIG. 2</b></p>  <p>The graph shows a bell-shaped curve representing the percentage of <math>sp^3</math> bonding as a function of total ion impinging energy in eV. The y-axis is labeled '% SP<sup>3</sup> BONDING' and the x-axis is labeled 'TOTAL ION IMPINGING ENERGY (eV)'. A vertical dashed line marks the peak of the curve at 100 eV on the x-axis. The curve starts at a low value, rises to the peak at 100 eV, and then gradually decreases as the energy increases further.</p> </div> <p>(‘331 patent at Fig. 2).</p> <p>Referring now to FIG. 2, there is shown a graphical depiction of percent <math>sp^3</math>-bonding in a deposited carbon layer as a function of total ion impinging energy. It has been demonstrated that the properties of amorphous-carbon films depend significantly on the fraction of <math>sp^3</math>-bonding. Additionally, as illustrated in FIG. 2, it is known that the percent <math>sp^3</math>-bonding is a predictable, and sensitive, function of total ion impinging energy. The maximum per cent <math>Sp^3</math>-bonding has been observed to occur at incident ion energies in the range of 30-150 e V. A high per cent <math>sp^3</math>-bonding corresponds to a high degree of diamond-like character of the amorphous carbon layer. Diamond-like carbon (DLC) materials are known to have, for example, low work functions and, therefore, are utilized in electron-emitting structures of electron emission devices, such as field emission devices. The data of FIG. 2 is utilized, in accordance with the method of the present invention, to accurately, and precisely, control and optimize the properties</p>

'399 Patent	U.S. Patent No. 5,837,331 ("331 Patent")
	<p data-bbox="646 270 1414 449">of amorphous multi-layered structure 100: a layer's property value is set, the corresponding percent <math>sp^3</math> -bonding is determined, and the corresponding total ion impinging energy specified. (‘331 patent at 4:30-50).</p> <div data-bbox="654 489 1333 888">  <p data-bbox="654 489 706 850"><math>U_s</math>   APPLIED VOLTAGE (VOLTS)</p> <p data-bbox="1141 856 1252 888">TIME (t)</p> </div> <p data-bbox="760 911 984 953"><b>FIG. 4</b></p> <p data-bbox="646 968 932 999">(‘331 patent at Fig. 4).</p> <div data-bbox="646 1041 1365 1377">  <p data-bbox="1101 1045 1157 1077">207</p> <p data-bbox="654 1146 706 1178">200</p> <p data-bbox="1027 1272 1084 1304"><u>201</u></p> </div> <p data-bbox="662 1444 935 1486"><b>FIG. 5</b></p> <p data-bbox="646 1501 932 1533">(‘331 patent at Fig. 5).</p> <p data-bbox="646 1577 1414 1896">Referring now to FIGS. 4 and 5, there are shown a graphical depiction (FIG. 4) of the step of modulating an applied voltage applied to a deposition substrate 201 (FIG. 5) in accordance with another embodiment of a method for forming an amorphous multi-layered structure 200 in accordance with the present invention. In this particular embodiment, the bias voltage applied to deposition substrate 201 is graded so that it varies smoothly and continuously with respect to time so that amorphous multi-layered</p>

'399 Patent	U.S. Patent No. 5,837,331 ("331 Patent")
	<p>structure 200 having graded properties is formed. In this particular embodiment amorphous multi-layered structure 200 is an amorphous carbon film, and the precursor of the multi-phase material is graphite. The applied voltage initially has a high value corresponding to a low %sp<sup>3</sup>. In this particular embodiment, the applied voltage is then decreased so that it has a parabolic functionality with respect to time, as illustrate in FIG. 4. The structure that is realized is shown in FIG. 5 which illustrates the gradient of %sp<sup>3</sup> over the thickness of amorphous multi-layered structure 200, the lowest relative sp<sup>3</sup> composition existing at the edge of amorphous multilayered structure 200 next to deposition substrate 201, the highest relative sp<sup>3</sup> composition existing at an outer surface 207 of amorphous multi-layered structure 200. It will occur to one skilled in the art to provide a bias voltage having other functionalities with respect to time so that the desired film properties are realized. ('331 patent at 5:64-6:22).</p>

'399 Patent	U.S. Patent No. 5,411,797 ("797 Patent")
<u>Claim 1</u>	
A hard carbon thin film arrangement comprising	The '797 Patent was filed on Apr. 1, 1993, and issued on May 2, 1995. This is prior to the '399 patent's priority date of Mar. 19, 1997.
a hard carbon thin film having a surface and	In the present application "nanophase diamond" has been used as a generic term for a material having some of the physical characteristics of diamond. In view of the physical properties of the materials produced in accordance with the present invention, the layer might alternatively be called diamond or "amorphous" diamond. (797 patent at 7:1-7).
an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and	<p>An electrode can be incorporated within the laser beam path to accelerate ions and trailing electrons away from the graphite foil target and toward the substrate. In addition, the electrode provides deceleration of the ions and trailing electrons at a point just before the ions and electrons are deposited upon the substrate. Acceleration and deceleration are achieved by electrical fields between the target and an electrode and between the electrode and substrate, respectively. Furthermore, a secondary electrode can be placed within the ion path and charged relative to the substrate so that the particles can be selectively placed at specific locations upon the substrate. Selective placement of particles provides in situ etching of the substrate during the deposition of the early layers of particles, increasing the strength of the bond of the nanophase diamond film with the substrate. (797 patent at 5:33-49).</p> <p>In the present application, the term "layer" has generally been used synonymously with coating or film, and connotes material deposited or grown on a substrate. The layer may include an interfacial layer in which the nanophase diamond film is chemically bonded to the substrate. Also, it should be understood that the substrate is not necessarily a different material than the layer, but merely serves as a collection source for material. Thus, the substrate might comprise diamond or nanophase diamond on which a layer of nanophase diamond is received to produce a homogeneous part of uniform physical properties. Furthermore, it is understood that the nanophase diamond film comprises substantially dehydrogenated nodules of <math>sp^3</math>-bonded carbon</p>

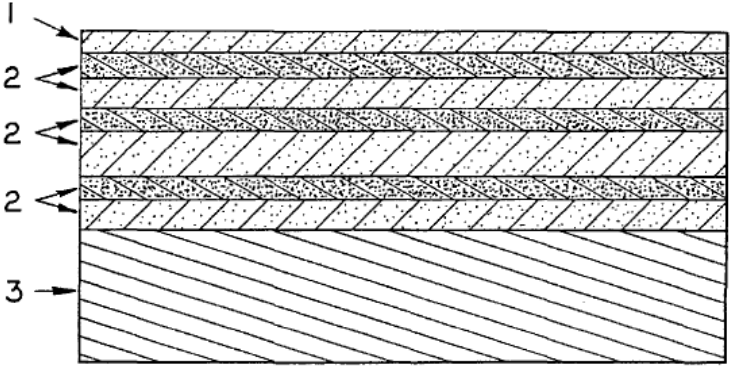
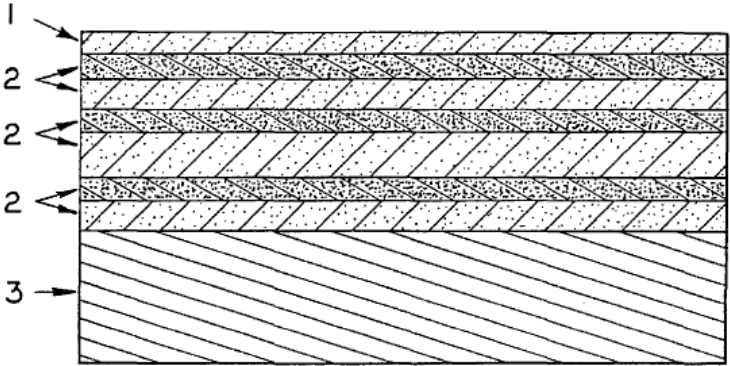
'399 Patent	U.S. Patent No. 5,411,797 ("797 Patent")
	<p>(i.e., fine-grained clusters having dimensions of 100-1000 angstroms and preferably less than 500 angstroms). ('797 patent at 6:52-68).</p> <p>The effect of compressive stress in a film is to generate a force tending to "pop" it off the surface to which it is applied. To produce a successful coating, a greater opposing force must be developed to hold the film onto</p> <p>the substrate. A number of techniques might be considered, but one of the best is simply to chemically bond the coating to the material it covers in an interfacial layer. One means of accomplishing this is by using the apparatus and method disclosed herein. The keV energies carried by the carbon ions created by the laser plasma source encourage the formation of an interfacial layer of 100 to 200 angstroms in thickness in which the nanophase diamond film is chemically bonded to the substrate. This enables the superior mechanical strength of the diamond layer to be used to protect the underlying substrate. In the archetypical case, nanophase diamond coatings on metal have been shown to provide significant advantages in reducing both friction and wear.</p> <p>The existence of a chemical bond to the substrate depends on the material selected for the substrate. In some cases, it may not be possible for the nanophase diamond to form a chemical bond with the substrate. In that case, the film will be bonded to the substrate with an alloyed layer of a thickness between about 5 and 50 nm. ('797 patent at 15:65-16:22).</p>
<p>having a graded carbon composition in which a ratio of <math>sp^2</math> to <math>sp^3</math> carbon-carbon bonding in said thin film decreases in said thickness direction from said interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<p>The term nanophase diamond generally may include nodules of diamond-bonded carbon containing anywhere from zero to 20% hydrogen concentration (although the nanophase diamond of the present invention is generally dehydrogenated at less than 5%). In addition, the films contain only insignificant amounts (preferably less than about 25%) of graphite (<math>sp^2</math>-bonded carbon) in the voids between the nodules. Thus, it is understood that the form of the material or the use of the term "nanophase diamond" indicates more than a specific type of composition (e.g., such as percentage of hydrogen or other impurities in interstitial sites in grain boundaries). The term "nanophase diamond"</p>

'399 Patent	U.S. Patent No. 5,411,797 ("797 Patent")
	<p>refers to any type of structure having nanometer-scale nodules of diamond-bonded carbon displaying characteristics similar to that of diamond ('797 patent at 7:7-22).</p> <p>It is believed, however, that the greatest diagnostic significance lies in the imaginary parts (loss) of the indices of refraction as shown in FIG. 4. It is believed that at small indices (less than 1.0 for a light wavelength of 632.8) the imaginary parts of the indices of refraction are approximately proportional to the fraction of <math>sp^2</math> bonding in the film, provided the real parts are reasonably constant. Purely diamond-like <math>sp^3</math> bonding would give no loss at these photon energies. It is believed that the curve labeled A in FIG. 4 is identified with an approximately 25% content of graphitic, <math>sp^2</math> bonds. See, N. Savvides, 58 <i>J. Appl. Phys.</i>, 518 (1985); 59 <i>J. Appl. Phys.</i>, 4133 (1986) (expressly incorporated herein by reference). The nanophase diamond films produced by the present invention are believed to have about 25% or less <math>sp^2</math> bonding, as shown in FIG. 4. Contrary to current belief, it is postulated that residual <math>sp^2</math> bonds are an artifact of production and are not necessary for stability of the remaining diamond-like <math>sp^3</math> bonding. Therefore, it is believed that a dehydrogenated nanophase diamond film can be grown by the apparatus of the present invention in which the <math>sp^2</math> bonding is minimal (on the order of 2% or less), resulting in characteristics approaching that of natural diamond. ('797 patent at 13:62-14:17).</p> <p>Yet another unique characteristic of the nanophase films of the present invention is the fact that the <math>ka</math> line energy of the carbon in the film approaches that of the carbon in natural diamond. A <math>ka</math> line energy, which is measurable with an x-ray spectrometer, results when the x-ray spectrum of the carbon in the film is excited with a focused electron beam on the film. The carbon in natural diamond has a different characteristic <math>Ka</math> line energy than does the carbon in graphite. It has been found that, due to the high proportion of <math>sp^3</math> bonding of the carbon within the film, the <math>ka</math> line energy of the carbon in the film is closer to that of the carbon in natural diamond than it is to that of the carbon in graphite; in other words, the <math>ka</math> line energy for the carbon in the nanophase diamond film of the present invention</p>

'399 Patent	U.S. Patent No. 5,411,797 ("797 Patent")
	<p>"approaches" that of the carbon in natural diamond. This is yet another indicator that the nanophase diamond film of the present invention is "diamondlike." Moreover, only one ka line energy is measurable. This is contrary to what would be expected if the film were simply a combination of diamond and graphite particles, which would result in two ka lines energies, each one corresponding to the carbon in each substance.</p> <p>('797 patent at 15:41-64).</p>



'399 Patent	U.S. Patent No. 6,080,470 ("470 Patent")
<u>Claim 1</u>	
A hard carbon thin film arrangement comprising	The '470 Patent was filed on Jun. 17, 1996, and issued on Jun. 27, 2000. This is prior to the '399 patent's priority date of Mar. 19, 1997.
a hard carbon thin film having a surface and	<div data-bbox="657 464 1382 825" data-label="Image"> </div> <p data-bbox="922 919 1084 972">FIG. 2</p> <p data-bbox="646 982 932 1014">('470 patent at Fig. 2).</p> <p data-bbox="646 1056 1419 1346">FIG. 2 is a schematic diagram showing an embodiment of a hierarchically structure of the carbon material of the invention, wherein the ratio between graphite-like <math>sp^2</math> bonds and diamond-like <math>sp^3</math> bonds is periodically modulated [Period of modulation is in the range of 10 nm to 1000 nm; (1)-soft upper layer, self lubricant, (2)-structure with periods of modulation, (3)-substrate]. ('470 patent at 4:59-65).</p>

'399 Patent	U.S. Patent No. 6,080,470 ("470 Patent")
<p>an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and</p>	<div data-bbox="657 275 1382 638">  <p>The diagram shows a cross-section of a material with five distinct layers. Layer 1 is the topmost layer, indicated by an arrow. Below it are three layers, each labeled '2' with an arrow. These layers have a stippled texture. The bottommost layer is labeled '3' with an arrow and has a diagonal hatching pattern.</p> </div> <p style="text-align: center;">FIG. 2</p> <p>Fig. 2</p> <p>FIG. 2 is a schematic diagram showing an embodiment of a hierarchically structure of the carbon material of the invention, wherein the ratio between graphite-like <math>sp^2</math> bonds and diamond-like <math>sp^3</math> bonds is periodically modulated [Period of modulation is in the range of 10 nm to 1000 nm; (1)-soft upper layer, self lubricant, (2)-structure with periods of modulation, (3)-substrate]. ('470 patent at 4:59-65).</p>
<p>having a graded carbon composition in which a ratio of <math>sp^2</math> to <math>sp^3</math> carbon-carbon bonding in said thin film decreases in said thickness direction from said interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<div data-bbox="657 1203 1382 1566">  <p>This diagram is identical to the one in the first row, showing layers 1, 2, 2, 2, and 3 with their respective textures and arrows.</p> </div> <p style="text-align: center;">FIG. 2</p> <p>('470 patent at Fig. 2).</p> <p>FIG. 2 is a schematic diagram showing an embodiment of a hierarchically structure of the carbon material of the invention, wherein the ratio between graphite-like <math>sp^2</math> bonds</p>

'399 Patent	U.S. Patent No. 6,080,470 ("470 Patent")
	<p>and diamond-like <math>sp^3</math> bonds is periodically modulated [Period of modulation is in the range of 10 nm to 1000 nm; (1)-soft upper layer, self lubricant, (2)-structure with periods of modulation, (3)-substrate]. (470 patent at 4:59-65).</p> <p>In accordance with the present invention, it is possible to synthesize a hierarchical structured material by gradually varying and/or modulating the ratio between the graphite-like <math>sp^2</math> carbon-carbon bonds and the diamond-like <math>sp^3</math> carbon-carbon bonds in a nanometer and/or micrometer scale, as shown in FIG. 2. The resultant structure possesses properties of increased flexibility and fracture strength, while exhibiting a decrease in intrinsic stress. Preferably, the ratio between the graphite-like <math>sp^2</math> carbon-carbon bonds and the diamond-like <math>sp^3</math> carbon-carbon bonds are periodically varied and/or modulated in the range of from about 10 nm to about 100 nm. It is also possible in accordance with the invention to synthesize the hierarchical material structure wherein the contents of the <math>sp^3</math> and <math>sp^2</math> carbon-carbon bonds, and/or carbide, silicide, and oxide bonds, between the carbon and alloying elements are gradually varied and/or modulated in nanometer and/or micrometer scale. (470 patent at 6:42-58).</p>

'399 Patent	“Noncrystalline Carbon Films With The Bonding And Properties Of Diamond” Collins, Davanloo; Pulsed Laser Deposition of Thin Films, 1994 (“Collins-PLDTF”)
<u>Claim 1</u>	
A hard carbon thin film arrangement comprising	The Collins-PLDTF reference was published 1994. This is prior to the '399 patent's priority date of Mar. 19, 1997.
a hard carbon thin film having a surface and	<p>In the classification of diamond films the most basic distinction is usually made between crystalline and noncrystalline compositions.<sup>1</sup> To date, the crystalline films have been the unique products of the techniques of chemical vapor deposition (CVD) and its variants, all of which utilize hydrogen in the growth process. Layers of noncrystalline materials often appear with the diamond crystals and those amorphous forms seem to be hard, carbon-rich plastics. Not only prepared with hydrogen, they retain substantial amounts which vary from 20% to 60% in the finished materials. Common usage has fixed the name diamondlike carbon (DLC) onto these materials, despite the preponderance of hydrogen in them.</p> <p>Another noncrystalline carbon has been prepared without hydrogen and found to have diamondlike properties as well. Termed amorphous diamond,<sup>2,3</sup> it was produced by accelerating and quenching an intense laser plasma of carbon ions onto a cold substrate.<sup>4,5</sup> The importance of this material was emphasized by reports<sup>2,3</sup> that it offered some unique advantages over DLC, and even over crystalline CVD films of diamond when used in infrared (IR) applications. (Collins-PLDTF at 7862).</p>
an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and	<p>As early as 1970, it was shown that the ablation of material by a focused laser beam produced a jetting of plasma equivalent to an ion beam of very high fluence. Last year Stevefelt <i>et al.</i><sup>12</sup> completed a modeling study which showed that significant fluxes of highly ionized carbon could be produced with kinetic energies of ke V by focused laser intensities in the range of <math>10^{11}</math>-<math>10^{12}</math> W cm<sup>-2</sup>. Typical results of these calculations are reproduced in Figs. 1 (a) and 1 (b). It can be seen that the dominant ions are C<sup>3+</sup> and C<sup>4+</sup> and that kinetic energies of 1 keV are readily attained. Such an ion source would seem to be appropriate for the production of overconstrained carbon nets from which layers of amorphous diamond could form. (Collins-PLDTF at 7863).</p>

'399 Patent	“Noncrystalline Carbon Films With The Bonding And Properties Of Diamond” Collins, Davanloo; Pulsed Laser Deposition of Thin Films, 1994 (“Collins-PLDTF”)
	<p>Substrates exposed to the ion fluxes emerging from the hotter core of the plasma are coated with amorphous diamond<sup>3</sup> while surfaces illuminated only by the cooler margins of the plasma grow layers of graphite, perhaps defected graphite as suggested by Tamor and Wu.<sup>3,14</sup> A planetary drive system for rotating substrates within the cone exposed only to ions from the plasma core insures the simultaneous deposition of uniform layers of amorphous diamond over several substrate disks 30 mm in diameter. (Collins-PLDTF at 7863).</p>
<p>having a graded carbon composition in which a ratio of <math>sp^2</math> to <math>sp^3</math> carbon-carbon bonding in said thin film decreases in said thickness direction from said interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<p>Theoretical considerations have suggested that amorphous diamond is not a single material but rather a category across which properties can vary. This has been most apparent in previous reports of the optical absorption coefficients measured for films produced under different conditions.<sup>2,3</sup> Greater intensities at the graphite feedstock have resulted in the formation of films with increased transparencies at visible wavelengths. This can be readily appreciated in the context of Fig. 1 (b) if it is assumed that the higher kinetic energies produced at elevated intensities drive carbon ions deeper into the layers previously deposited to create higher densities, greater overconstraint, and ultimately, a conversion of more material into <math>sp^3</math> nodules. (Collins-PLDTF at 7864).</p> <p>The correlations of absorption coefficient, density, and electrical resistivity with increased ion energies are completely consistent with the model for the condensation of nodules in which carbon atoms are linked with diamondlike <math>sp^3</math> bonds. The relationship between <math>n_i</math> and the fraction of <math>sp^3</math> bonding of a pure carbon system has already been convincingly demonstrated.<sup>2,3,5,15-17</sup> A benchmark value of <math>n_i = 0.3</math> has been identified<sup>16,17</sup> with an <math>sp^3</math> content of 75%. Increased fractions of <math>sp^3</math> lead to lower values of <math>n_i</math> and the particular <math>n_i = 0.16</math> mentioned above indicates a diamond content approaching 87%.</p> <p>A crude model of amorphous diamond could be comprised of a packing of spheres of uniform size which would account for 74% of the volume.<sup>18</sup> The remaining 26% void could be filled with carbon bonded by mixtures of <math>sp^2</math> and <math>sp^3</math>. If the spheres were <math>sp^3</math> nodules at the density of diamond and the</p>

'399 Patent	<b>“Noncrystalline Carbon Films With The Bonding And Properties Of Diamond” Collins, Davanloo; Pulsed Laser Deposition of Thin Films, 1994 (“Collins-PLDTF”)</b>
	<p>intergranular spaces were filled with graphite, an effective density of <math>3.2 \text{ g cm}^{-3}</math> would be realized. The inclusion of smaller spheres of diamond would provide a range of accessible densities from 3.2 to <math>3.5 \text{ g cm}^{-3}</math>. Of course, a poor packing of the spheres together with some irregularity of shapes would tend to blur the lower limit. Figure 3 plots the resulting data for films deposited at the highest ablation intensities together with values of density that would result if the voids in the model were filled with nothing, graphite, and diamond, respectively. At these higher intensities there was enough variability that results are best presented as a histogram showing the number of times films were produced at the different values of density we could resolve. Recognizing that the most probable packing is not ideal nor the sizes uniform suggests that the voids are most often filled with carbon atoms linked by graphitic <math>sp^3</math> bonding. However, unless there are phases included that are more dense than natural diamond, the diamond content of the films shown in Fig. 3 must be at least the 74% value characteristic of the fraction of a volume which can be filled with closely packed spheres. This is in good agreement with the <math>sp^3</math> fraction indicated by measurements of <math>n_i</math>.</p> <p>(Collins-PLDTF at 7864-7865).</p>

'399 Patent	U.S. Patent No. 4,777,090 ("090 Patent")
<u>Claim 1</u>	
A hard carbon thin film arrangement comprising	The '090 patent was filed on Nov. 3, 1986 and issued on Oct. 11, 1988. This is greater than one year before the '399 patent's priority date of Mar. 19, 1997.
a hard carbon thin film having a surface and	<p>For example, in the case of an amorphous carbon to diamond coating, the coating is substantially amorphous in contact with the substrate, and substantially ordered, as microcrystalline or poly-crystalline, remote from the substrate. ( '090 patent at 2:28-32).</p> <p>According to one exemplification the coating is formed of amorphous carbon at the substrate and either (1) ordered carbon or (2) silicon dioxide remote therefrom. At the coating-substrate interface, the coating is substantially amorphous, characterized by the substantial absence of long range order although it may include more ordered regions and even crystalline or polycrystalline regions therein. ( '090 patent at 4:60-67).</p>
an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and	<p>The coating has a relatively disordered portion at the substrate-coating interface and a relatively ordered portion remote from the substrate-coating interface. ( '090 patent at Abstract).</p> <p>They have an adherent, abrasion resistant, substantially transparent coating that is graded in composition and/or structure from amorphous carbon at its interface with the plastic substrate to ordered carbon e.g., diamond like or even diamond, remote therefrom or to silicon dioxide remote from the substrate - amorphous carbon interface. ( '090 patent at 2:52-58).</p> <p>According to one exemplification the coating is formed of amorphous carbon at the substrate and either (1) ordered carbon or (2) silicon dioxide remote therefrom. At the coating-substrate interface, the coating is substantially amorphous, characterized by the substantial absence of long range order although it may include more ordered regions and even crystalline or polycrystalline regions therein. The coating is graded in composition and/or structure remote from the substrate. ( '090 patent at 4:60-68).</p>



'399 Patent	U.S. Patent No. 4,777,090 ("090 Patent")
	<p>In an alternative exemplification the coating is carbon, matched in properties to an amorphous semiconductor substrate such as a photovoltaic device on electrophotographic drum, at the interface therewith, and graded to a diamond surface having a predominance of tetrahedral <math>Sp^3</math> bonding remote from the semiconductor substrate. ( '090 patent at 5:13-18).</p> <p>According to a still further exemplification the substrate may be a metal substrate or a semiconductor substrate, e.g., a soft metal substrate, as an aluminum or copper substrate, or an amorphous alloy of silicon, where the coating is an amorphous material in contact with the substrate and an ordered material therefrom. Thus, an amorphous silicon body may carry a carbon coating that is substantially amorphous at the silicon - carbon interface, and substantially tetrahedrally coordinated, diamond-like or diamond carbon remote therefrom. ( '090 patent at 8:14-24).</p> <p>The herein contemplated, transparent protective layer 570 provides an added measure of durability and toughness. It is graded in composition and/ or structure, i.e., from amorphous carbon at its interface with the top blocking layer 558 to either amorphous <math>SiO_2</math> or diamond remote therefrom. ( '090 patent at 10:17-22).</p> <p>(b) an adherent, abrasion resistant coating thereon substantially amorphous and consisting essentially of carbon at the substrate-coating interface, graded in composition remote from the substrate-coating interface, and consisting essentially of one or more of C, or silicon dioxide, and mixtures thereof, where the compositionally graded material remote from the substrate-coating interface comprises <math>SiO_x</math> where x is from 1.60 to 2.00. ( '090 patent at 10:33-41).</p>
having a graded carbon composition in which a ratio of $sp^2$ to $sp^3$ carbon-carbon bonding in said thin film decreases in said thickness direction from said	The microwave deposition of a carbon-diamond or carbon-silicon dioxide coating having graded order or composition allows a relatively thick but substantially colorless coating to be applied to a substrate that is mis-matched in a physical parameter, as modulus of elasticity, coefficient of thermal



'399 Patent	U.S. Patent No. 4,777,090 ("090 Patent")
<p>interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<p>expansion, lattice parameter, size of microcrystalline inclusions, or volume fraction of microcrystalline material, to be deposited quickly and without deformation or degradation of the substrate or delamination of the coating. ('090 patent at 4:32-41).</p> <p>The coating is graded in composition and/or structure remote from the substrate. In the case of an amorphous carbon to diamond coating, it is ordered remote from the substrate, e.g., microcrystalline or polycrystalline remote from the substrate. The ordered portion of the coating structurally comprises carbon in tetrahedrally coordinated, diamond like or even diamond structure, characterized by a predominance of <math>sp^3</math> bonding.</p> <p>In the case of coating graded from amorphous carbon to diamond, the <math>sp^3</math> bonding combined with the unique microwave method of application results in a particularly hard coating that is substantially colorless, and abrasion resistant, on a plastic substrate.</p> <p>In an alternative exemplification the coating is carbon, matched in properties to an amorphous semiconductor substrate such as a photovoltaic device on electrophotographic drum, at the interface therewith, and graded to a diamond surface having a predominance of tetrahedral <math>Sp^3</math> bonding remote from the semiconductor substrate. ('090 patent at 4:67-5:19).</p> <p>The thickness of the gradation from amorphous at the substrate to crystalline carbon, e.g., diamond, or to silicon dioxide, remote from the substrate is a function of, inter alia, the degree of mis-match of the properties, i.e., lattice parameters, coefficients of elasticity, or thermal expansion coefficients, of the substrate and the hard coating, and may be from several atomic diameters to several microns. ('090 patent at 5:24-31).</p> <p>In the case of deposition of diamond atop amorphous carbon, the pressure is increased during the high micro wave energy phase. ('090 patent at 6:57-59).</p> <p>According to a still further exemplification the substrate may be a metal substrate or a semiconductor substrate, e.g., a soft</p>

'399 Patent	U.S. Patent No. 4,777,090 ("090 Patent")
	<p>metal substrate, as an aluminum or copper substrate, or an amorphous alloy of silicon, where the coating is an amorphous material in contact with the substrate and an ordered material therefrom. Thus, an amorphous silicon body may carry a carbon coating that is substantially amorphous at the silicon - carbon interface, and substantially tetrahedrally coordinated, diamond-like or diamond carbon remote there from. ( '090 patent at 8:14-24).</p> <p>The herein contemplated, transparent protective layer 570 provides an added measure of durability and toughness. It is graded in composition and/ or structure, i.e., from amorphous carbon at its interface with the top blocking layer 558 to either amorphous SiO<sub>2</sub> or diamond remote therefrom. ( '090 patent at 10:17-22).</p> <p>(b) an adherent, abrasion resistant coating thereon substantially amorphous and consisting essentially of carbon at the substrate-coating interface, graded in composition remote from the substrate-coating interface, and consisting essentially of one or more of C, or silicon dioxide, and mixtures thereof, where the compositionally graded material remote from the substrate-coating interface comprises SiO<sub>x</sub> where x is from 1.60 to 2.00. ( '090 patent at 10:33-41).</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
<u>Claim 1</u>	
A hard carbon thin film arrangement comprising	The '677 patent was filed on Feb. 18, 1986 and issued on Oct. 31, 1989. This is greater than one year before the '399 patent's priority date of Mar. 19, 1997.
a hard carbon thin film having a surface and	<p>In order to achieve the above-mentioned object, a wear-protected device in accordance with the present invention has a hard film containing at least carbon on at least a surface to receive physical action, and thereon a lubricative film which has a smaller friction coefficient than that of the hard carbon film. In another embodiment of the present invention, on at least a surface to receive a physical action of a substrate, a hard film containing at least carbon is applied with a buffer film which has good bonding force both to the substrate and the hard film. ( '677 patent at 1:42-52).</p> <p>The above-mentioned wear-protected device is made by disposing a substrate in a direction substantially parallel with direction of an ion-beam which irradiates a carbon target, in an ion-beam sputtering apparatus, and then carrying out the ion-beam irradiation on said carbon target, to form a hard carbon film on the substrate. ( '677 patent at 1:53-58).</p> <p>As shown in FIG. 1, on a surface to receive physical action of a substrate, such as a glass lens, a metal sheet of a hard magnetic disk or a plastic film of a magnetic video tape, etc., a hard carbon film 12 is provided by an ion-beam sputtering process. Then, on the surface of the carbon hard film 12, a lubricative film 13 which has a smaller friction coefficient than that of the carbon hard film 12 is provided in order to protect the surface of the substrate 11 to receive the physical action permanently from abrasion due to the physical action, such as mechanical friction by a magnetic head. ( '677 patent at 2:23-33).</p> <p>As the lubricative film 13, when a film which contains at least carbon is used, but the hydrogen concentration thereof is equal or smaller than that of the hard carbon film 12, the lubricative film has a stronger bonding force to the hard carbon film 12. ( '677 patent at 2:37-41).</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>By selecting the thickness of the carbon hard film 12 to be less than 500 Å, effect to the substrate can be minimized and the bonding force on the substrate becomes large and stable. ('677 patent at 2:54-57).</p> <p>For instance, when on a magnetic film as the substrate a hard carbon film 12 of 200 Å thickness is formed, and further thereon a lubricative film 13 of 100 Å is coated, even though they are on a flexible substrate, the device operates stable enough without mechanical damage, and no adverse effect on the magnetic characteristic is observed. ('677 patent at 2:62-68).</p> <p>FIG. 2 shows time change of friction coefficient measured at repeated impressions of a 10 g weight, scanning at a speed of 1.00 sec on a wear-protected device, which is made by using polymethylacrylate (PMMA) resin as the substrate, and thereon a hard carbon film 12 of about 300 Å is formed, and further thereon, as the lubricative film 13 a film containing at least carbon and wherein the hydrogen component is smaller than that of the hard carbon film 12 is formed to a thickness of about 200 Å. ('677 patent at 3:1-10).</p> <p>An actual example of wear-protected device embodying the present invention is shown in FIG. 5. On a rough surface of a substrate 11, which has unevenness of about 1000 Å, a hard carbon 12 containing diamond granules of about 2000Å is formed, and further thereon, as a lubricative 13, for instance, a hard carbon film of about 1000 Å thickness is formed ('677 patent at 4:8-14).</p> <p>A second embodiment of the present invention is shown in FIG. 3. On at least a surface to receive physical action such as pressing force, friction force, etc., a hard carbon film 11 is formed with providing a buffer film 31 between the substrate 11 and the hard carbon film 12. Therefore, the bonding force between the hard carbon film 12 and the substrate 11 is increased, and made stable. By using a film which contains at least carbon and wherein the hydrogen component is equal to or less than the hard carbon film as the buffer film 21, there is a possibility of further increasing the bonding force onto the substrate 11.</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>( ' 677 patent at 3:26-37).</p> <p>For instance, when surface protection of a plastic lens is made by embodying the present invention, as a result of stably bonding a high hardness thin film, such as hard carbon film, on a low hardness substrate, such as a plastic lens, a wear-protected device having sufficient strength and long life against scratch damage or a like defect, is obtainable on top of the low friction characteristic. ( ' 677 patent at 3:47-54).</p> <p>A third embodiment of the present invention is shown in FIG. 4, wherein on at least a surface to receive a physical action of the substrate, a buffer layer 31 comprising at least carbon and hydrogen is formed in a manner that hydrogen component distribution changes, gradually increasing, to that of the hard carbon film 12. ( ' 677 patent at 3:55-60).</p> <p>By Raman spectroscopic analysis it was confirmed that the structures of the lubricative film 13 and the buffer film 31 are of graphite-like carbon and that of the hard carbon film 12 is of diamond-like carbon. The Vickers hardness of the hard carbon film 12 was more than 3000 Kg/cm<sup>2</sup>. ( ' 677 patent at 4:61-66).</p> <p>On a disk of a polyester film 71 of about 50 μm thickness, a magnetic film 72 for information storage is formed with Co-Cr alloy of 1 μm by a known process; and further on the surface of the magnetic film 72, a hard carbon film 12 of about 100 Å thickness is formed by the above-mentioned process; and further on the surface of the hard carbon film 12, a lubricative film 13 of about 100 Å thickness is formed by the above-mentioned process. The resultant magnetic data disk can enjoy a very long lifetime in comparison with the conventional magnetic disk wherein the hard carbon film 12 and the lubricative film 13 are not formed; and the formation of the above-mentioned wear-protective layers do not effect the magnetic recording characteristics, but is advantageous in reducing friction between the surface of the magnetic disk and a magnetic head to be applied thereto for information storing or/reading. ( ' 677 patent at 5:8-25).</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>a hard carbon film formed on said substrate by ion irradiation, said hard carbon film consisting essentially of carbon or carbon and hydrogen, and ( '677 patent at 5:33-35).</p> <p>6. A wear-protected device in accordance with claim 1, wherein said hard carbon film is a carbon film containing diamond granules of sizes of less than 1 <math>\mu\text{m}</math>. ( '677 patent at 5:65-68).</p> <p>a hard carbon film formed on said buffer film by ion irradiation, said hard carbon film consisting essentially of carbon or carbon and hydrogen. ( '677 patent at 6:14-16).</p> <p>10. A wear-protected device in accordance with claim 8, wherein said hard carbon film has a thickness of less than 500 Å. ( '677 patent at 6:22-25).</p> <p>a hard carbon film layer formed on said buffer film layer; and a hydrogen-containing lubricative film formed on said hard carbon film; said buffer film layer comprising at least carbon and hydrogen and having a hydrogen concentration which gradually increases towards said hard carbon film; concentration of hydrogen in said lubricative film gradually decreasing from that on an outer surface of said hard carbon film to that on an outer surface of said lubricative film layer. ( '677 patent at 6:45-56).</p> <p>a hard carbon film formed on said buffer film by ion irradiation, said hard carbon film consisting essentially of carbon or carbon and hydrogen, and ( '677 patent at 6:66-68).</p> <p>a hard carbon film formed on said surface by ion beam sputtering, said hard carbon film being less than 500 Å in thickness and consisting essentially of carbon or carbon and hydrogen, said hard carbon film having a diamond structure with a Vickers hardness or more than 3000 Kg/cm<sup>2</sup>; and ( '677 patent at 7:10-15).</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>a hard carbon film formed on said buffer layer by ion beam sputtering, said hard carbon film being less than 500 Å in thickness and consisting essentially of carbon or carbon and hydrogen, said hard carbon film having a diamond structure with a Vickers hardness or more than 3000 Kg/cm<sup>2</sup>; and ('677 patent at 8:4-9).</p>
<p>an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and</p>	<p>In another embodiment of the present invention, on at least a surface to receive a physical action of a substrate, a hard film containing at least carbon is applied with a buffer film which has good bonding force both to the substrate and the hard film. ( '677 patent at 1:47-52).</p> <p>A second embodiment of the present invention is shown in FIG. 3. On at least a surface to receive physical action such as pressing force, friction force, etc., a hard carbon film 11 is formed with providing a buffer film 31 between the substrate 11 and the hard carbon film 12. Therefore, the bonding force between the hard carbon film 12 and the substrate 11 is increased, and made stable. By using a film which contains at least carbon and wherein the hydrogen component is equal to or less than the hard carbon film as the buffer film 21, there is a possibility of further increasing the bonding force onto the substrate 11. By selecting the thickness of the buffer film 21 to be less than 500 Å, sufficient and stable bonding of the hard carbon film 12 on the substrate is achieved, and the high hardness surface is bonded more stably with respect to external pressing force, and strain the film is minimized. ( '677 patent at 3:26-42).</p> <p>For instance, in case of making a wear-protected device as shown in FIG. 4, a carbon target 61 in a sputtering chamber 60 is sputtered by an ion-beam of argon gas having ion energy of 1.2 eV and 60 mA generated by an ion-beam source 62. Thereby, a buffer film 31 of about 100 Å thickness is formed on the substrate 11. Thereafter, by gradually increasing hydrogen component in the argon gas in the chamber 60, a buffer film 31 of carbon is completed. ( '677 patent at 4:24-32).</p> <p>A third embodiment of the present invention is shown in</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>FIG. 4, wherein on at least a surface to receive a physical action of the substrate, a buffer layer 31 comprising at least carbon and hydrogen is formed in a manner that hydrogen component distribution changes, gradually increasing, to that of the hard carbon film 12. ( '677 patent at 3:55-60).</p> <p>By Raman spectroscopic analysis it was confirmed that the structures of the lubricative film 13 and the buffer film 31 are of graphite-like carbon and that of the hard carbon film 12 is of diamond-like carbon. The Vickers hardness of the hard carbon film 12 was more than 3000 Kg/cm<sup>2</sup>. ( '677 patent at 4:61-66).</p> <p>The graphite-like carbon film appears to be suitable as the buffer film 31 and the lubricative film 13 because of its less hard characteristic than the diamond like carbon, while the diamond-like carbon film appears to be suitable as the hard carbon film 12 because of its hard characteristics. ( '677 patent at 4:67-5:4).</p> <p>a buffer film formed on said substrate, said buffer film comprising at least carbon and hydrogen, the distribution of said hydrogen being sloped in concentration, and ( '677 patent at 6:10-13).</p> <p>9. A wear-protected device in accordance with claim 8, wherein said buffer film is of a substance containing at least carbon and hydrogen, component thereof is smaller than that in said carbon film. ( '677 patent at 6:17-21).</p> <p>13. A wear-protected device in accordance with claim 8, wherein: the hydrogen in said buffer film increases in concentration towards said hard carbon film. ( '677 patent at 6:33-36).</p> <p>a buffer film layer formed on said substrate; a hard carbon film layer formed on said buffer film layer; and a hydrogen-containing lubricative film formed on said hard carbon film; said buffer film layer comprising at least carbon and hydrogen and having a hydrogen concentration which gradually increases towards said hard carbon film; ( '677 patent at 6:44-52).</p>



'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>a buffer film formed on said substrate, said buffer film comprising at least carbon and hydrogen, the distribution of said hydrogen being sloped in concentration, ('677 patent at 6:62-65).</p> <p>a buffer layer formed on said surface, said buffer layer being less than 500 Å in thickness and consisting essentially of carbon or carbon and hydrogen, said ('677 patent at 7:37-39).</p> <p>19. The wear-protected structure of claim 18, wherein: said lubricative film consists essentially of carbon and hydrogen; and said buffer layer, said hard carbon film and said lubricative film collectively have a profile of hydrogen content which gradually increases through the thickness of said buffer layer towards said hard carbon layer, remains generally constant through the thickness of said hard carbon layer, and gradually decreases through the thickness of said lubricative film away from said hard carbon layer. ('677 patent at 8:27-38).</p>
<p>having a graded carbon composition in which a ratio of <math>sp^2</math> to <math>sp^3</math> carbon-carbon bonding in said thin film decreases in said thickness direction from said interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<div data-bbox="665 1081 1412 1438"> </div> <p>( '677 patent at Figure 4, 4A).</p> <p>A second embodiment of the present invention is shown in FIG. 3. On at least a surface to receive physical action such as pressing force, friction force, etc., a hard carbon film 11 is formed with providing a buffer film 31 between the substrate 11 and the hard carbon film 12. Therefore, the bonding force between the hard carbon film 12 and the substrate 11 is increased, and made stable. By using a film which contains at least carbon and wherein the hydrogen component is equal to or less than the hard carbon film as the buffer film 21, there is a possibility of further increasing the bonding force</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>onto the substrate 11. By selecting the thickness of the buffer film 21 to be less than 500 Å, sufficient and stable bonding of the hard carbon film 12 on the substrate is achieved, and the high hardness surface is bonded more stably with respect to external pressing force, and strain the film is minimized. ( '677 patent at 3:26-42).</p> <p>For instance, in case of making a wear-protected device as shown in FIG. 4, a carbon target 61 in a sputtering chamber 60 is sputtered by an ion-beam of argon gas having ion energy of 1.2 eV and 60 mA generated by an ion-beam source 62. Thereby, a buffer film 31 of about 100 Å thickness is formed on the substrate 11. Thereafter, by gradually increasing hydrogen component in the argon gas in the chamber 60, a buffer film 31 of carbon is completed. The mixing of hydrogen gas in the argon gas is increased gradually up to about 50% of H<sub>2</sub> concentration in a manner of five-step-divided injections of the hydrogen the buffer film 31 is formed. Thereafter, with retaining the hydrogen component of 50% a hard carbon film 12 of about 200 Å thickness is formed. ( '677 patent at 4:24-38).</p> <p>By using a film which contains at least carbon and wherein the hydrogen component is equal to or less than the hard carbon film as the buffer film 21, there is a possibility of further increasing the bonding force onto the substrate 11. ( '677 patent at 3:33-37).</p> <p>A third embodiment of the present invention is shown in FIG. 4, wherein on at least a surface to receive a physical action of the substrate, a buffer layer 31 comprising at least carbon and hydrogen is formed in a manner that hydrogen component distribution changes, gradually increasing, to that of the hard carbon film 12. ( '677 patent at 3:55-60).</p> <p>By Raman spectroscopic analysis it was confirmed that the structures of the lubricative film 13 and the buffer film 31 are of graphite-like carbon and that of the hard carbon film 12 is of diamond-like carbon. The Vickers hardness of the hard carbon film 12 was more than 3000 Kg/cm<sup>2</sup>. ( '677 patent at 4:61-66).</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>The graphite-like carbon film appears to be suitable as the buffer film 31 and the lubricative film 13 because of its less hard characteristic than the diamond like carbon, while the diamond-like carbon film appears to be suitable as the hard carbon film 12 because of its hard characteristics. ( '677 patent at 4:67-5:4).</p> <p>a buffer film formed on said substrate, said buffer film comprising at least carbon and hydrogen, the distribution of said hydrogen being sloped in concentration, and ( '677 patent at 6:10-13).</p> <p>9. A wear-protected device in accordance with claim 8, wherein said buffer film is of a substance containing at least carbon and hydrogen, component thereof is smaller than that in said carbon film. ( '677 patent at 6:17-21).</p> <p>13. A wear-protected device in accordance with claim 8, wherein: the hydrogen in said buffer film increases in concentration towards said hard carbon film. ( '677 patent at 6:33-36).</p> <p>a buffer film layer formed on said substrate; a hard carbon film layer formed on said buffer film layer; and a hydrogen-containing lubricative film formed on said hard carbon film; said buffer film layer comprising at least carbon and hydrogen and having a hydrogen concentration which gradually increases towards said hard carbon film; ( '677 patent at 6:44-52).</p> <p>a buffer film formed on said substrate, said buffer film comprising at least carbon and hydrogen, the distribution of said hydrogen being sloped in concentration, ( '677 patent at 6:62-65).</p> <p>a buffer layer formed on said surface, said buffer layer being less than 500 Å in thickness and consisting essentially of carbon or carbon and hydrogen, said ( '677 patent at 7:37-39).</p> <p>19. The wear-protected structure of claim 18, wherein: said lubricative film consists essentially of carbon and hydrogen;</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>and said buffer layer, said hard carbon film and said lubricative film collectively have a profile of hydrogen content which gradually increases through the thickness of said buffer layer towards said hard carbon layer, remains generally constant through the thickness of said hard carbon layer, and gradually decreases through the thickness of said lubricative film away from said hard carbon layer. ( '677 patent at 8:27-38).</p> <p>As the lubricative film 13, when a film which contains at least carbon is used, but the hydrogen concentration thereof is equal or smaller than that of the hard carbon film 12, the lubricative film has a stronger bonding force to the hard carbon film 12. ( '677 patent at 2:37-41).</p> <p>resin as the substrate, and thereon a hard carbon film 12 of about 300 Å is formed, and further thereon, as the lubricative film 13 a film containing at least carbon and wherein the hydrogen component is smaller than that of the hard carbon film 12 is formed to a thickness of about 200 Å. ( '677 patent at 3:5-10).</p> <p>When a lubricative film 13 is formed on the surface of the hard carbon film 12, the hydrogen component distribution thereof is gradually decreased from a component equal to that one the surface of the hard carbon film 12 down to a low component of the surface of the lubricative layer 13. ( '677 patent at 3:61-66).</p> <p>2. A wear-protected device in accordance with claim 1, wherein said lubricative film is made of a substance containing carbon and having a hydrogen component which is smaller than that in said hard carbon film. ( '677 patent at 5:39-43).</p> <p>5. A wear-protected device in accordance with claim 1, wherein said lubricative film is of a substance containing at least carbon and hydrogen, component thereof gradually decreasing from a component equal to that of said hard carbon film at the part said lubricative film contacting said hard carbon film to a component of a surface at which said lubricative film receives external physical action. ( '677 patent at 5:56-64).</p>

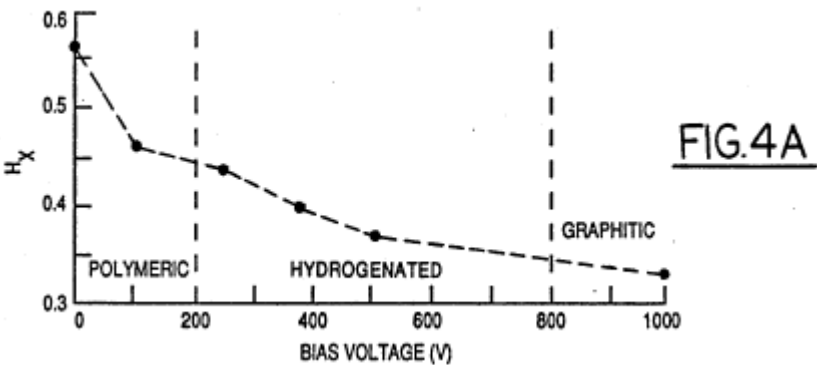
'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	<p>concentration of hydrogen in said lubricative film gradually decreasing from that one an outer surface of said hard carbon film to that one an outer surface of said lubricative film layer. ( '677 patent at 6:53-56).</p> <p>a solid state lubricative film formed on an opposite surface of said hard carbon film from said substrate, said lubricative film being less than 500 Å in thickness, having a coefficient of friction on an exposed outer surface thereof which is both less than 0.3 and less than the coefficient of friction of said surface of said hard carbon film; said lubricative film, if containing carbon, containing no more hydrogen by weight percent, than does said hard carbon film; and said lubricative film consisting essentially of at least one constituent selected from the group: graphitic-structure carbon, carbon with up to 50 percent hydrogen ZrS<sub>2</sub>, VS<sub>2</sub>, MoS<sub>2</sub>, WS<sub>2</sub>, PeS<sub>2</sub>, WSe<sub>2</sub>, MoSe<sub>3</sub>, NbSe<sub>2</sub>, a compound of tellurium, a fluorine compound having the general formula (CF<sub>x</sub>)<sub>n</sub>, CdCl<sub>2</sub>, CdI<sub>2</sub>, BN and mica. ( '677 patent at 7:16-31).</p> <p>a solid state lubricative film formed on an opposite surface of said hard carbon film from said buffer layer, said lubricative film being less than 500 Å in thickness, having a coefficient of friction on an exposed outer surface thereof which is both less than 0.3 and less than the coefficient of friction of said surface of said hard carbon film; said lubricative film, if containing carbon, containing no more hydrogen, by weight percent, than does said lubricative film, if containing carbon, containing no more hydrogen, by weight percent, than does said hard carbon film; and said lubricative film consisting essentially of at least one constituent selected from the group: graphitic-structure carbon, carbon with up to 50 percent hydrogen, ZrS<sub>2</sub>, VS<sub>2</sub>, MoS<sub>2</sub>, WS<sub>2</sub>, PeS<sub>2</sub>, WSe<sub>2</sub>, MoSe<sub>3</sub>, NbSe<sub>2</sub>, a compound of tellurium, a fluorine compound having the general formula (CF<sub>x</sub>)<sub>n</sub>, CdCl<sub>2</sub>, CdI<sub>2</sub>, BN and mica. ( '677 patent at 8:10-26).</p> <p>19. The wear-protected structure of claim 18, wherein: said lubricative film consists essentially of carbon and hydrogen; and said buffer layer, said hard carbon film and said</p>

'399 Patent	U.S. Patent No. 4,877,677 ("677 Patent")
	lubricative film collectively have a profile of hydrogen content which gradually increases through the thickness of said buffer layer towards said hard carbon layer, remains generally constant through the thickness of said hard carbon layer, and gradually decreases through the thickness of said lubricative film away from said hard carbon layer. ('677 patent at 8:27-38).

'399 Patent	U.S. Patent No. 5,237,967 ("967 Patent")																
<u>Claim 1</u>																	
A hard carbon thin film arrangement comprising	The '967 patent was filed on Jan. 8, 1993 and issued on Aug. 24, 1993. This is greater than one year before the '399 patent's priority date of Mar. 19, 1997.																
a hard carbon thin film having a surface and	<p>More particularly, the invention relates to a component having a hard, wear resistant coating of an amorphous hydrogenated carbon film formed thereupon. ( '967 patent at 1:9-12).</p> <p>The present invention discloses a powertrain component, such as a valve lifter, or journal or engine bearing for use in an internal combustion engine and a method for applying a hard, wear resistant film which firmly adheres to the component. The present invention also discloses a powertrain component with an amorphous hydrogenated carbon film which significantly reduces friction and wear. Also disclosed is an interlayer system for improving adherence and ability to withstand mechanical stresses. ( '967 patent at 2:29-38).</p> <p>Accordingly, an object of the present invention is to provide a powertrain component such as a valve lifter for use in an internal combustion engine and a method for applying a hard, wear resistant film which firmly adheres to the component. In such an environment, an amorphous, hydrogenated carbon film is formed thereupon to impart the characteristics of low friction and wear resistance. ( '967 patent at 2:63-3:2).</p> <div data-bbox="602 1304 1421 1665"> <table border="1"> <caption>Data points estimated from FIG. 4A</caption> <thead> <tr> <th>Bias Voltage (V)</th> <th>Hx</th> </tr> </thead> <tbody> <tr><td>0</td><td>0.58</td></tr> <tr><td>100</td><td>0.48</td></tr> <tr><td>200</td><td>0.45</td></tr> <tr><td>400</td><td>0.40</td></tr> <tr><td>600</td><td>0.38</td></tr> <tr><td>800</td><td>0.36</td></tr> <tr><td>1000</td><td>0.34</td></tr> </tbody> </table> </div> <p>( '967 patent at Figure 4A).</p>	Bias Voltage (V)	Hx	0	0.58	100	0.48	200	0.45	400	0.40	600	0.38	800	0.36	1000	0.34
Bias Voltage (V)	Hx																
0	0.58																
100	0.48																
200	0.45																
400	0.40																
600	0.38																
800	0.36																
1000	0.34																

'399 Patent	U.S. Patent No. 5,237,967 ("967 Patent")														
	<div data-bbox="581 283 1393 724" data-label="Figure"> <table border="1"> <caption>Data points for FIG. 4B</caption> <thead> <tr> <th>Bias Voltage (V)</th> <th>Hardness (GPa)</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>13</td> </tr> <tr> <td>200</td> <td>16</td> </tr> <tr> <td>400</td> <td>14</td> </tr> <tr> <td>600</td> <td>11</td> </tr> <tr> <td>800</td> <td>8</td> </tr> <tr> <td>1000</td> <td>6</td> </tr> </tbody> </table> </div> <p data-bbox="565 762 906 800">('967 patent at Figure 4B).</p> <p data-bbox="565 835 1442 1346">The mechanical properties of amorphous hydrogenated carbon films, e.g. hardness, elastic modulus, Poisson's ratio, etc. depend on the bias voltage, in addition to the type of hydrocarbon gas used during deposition. The hardness of the films deposited at different bias voltages is shown in FIG. 4B. Hardness reaches a peak, about 16 GPa--as measured by nanoindentation techniques--for hydrogenated carbon films deposited at 200-250 rms bias voltage. Such hardness values are substantially equivalent to 30 GPa when measured by more conventional methods, such as the Vickers test. Hardness decreases monotonically at higher bias voltages. The high hardness of hydrogenated carbon films probably arises from an over-constrained extended network in which small graphitic clusters are captured. The durability of hydrogenated carbon films is optimal at bias voltages ranging from 200 v to 800 v rms.</p> <p data-bbox="565 1381 1442 1749">As noted earlier, hydrogenated carbon films deposited by CVD typically contain large compressive stresses which may sometimes cause buckling of the film. The compressive stress exerted by the film is illustrated in FIG. 4C. The stress is small for polymer-like films, increases to a maximum near 50 v, then decreases monotonically and almost vanishes at 1000 v. As with observations noted earlier, without wishing to be bound by any particular theory, it appears that the decrease in stress may be related to reduced hydrogen content and a transition from an amorphous to a graphite-like morphology with increasing bias voltage.</p> <p data-bbox="565 1785 1442 1892">The disclosed films may be usefully applied to various components, such as engine and journal bearings, besides a valve stem and a valve guide. Other applications include the use of</p>	Bias Voltage (V)	Hardness (GPa)	0	13	200	16	400	14	600	11	800	8	1000	6
Bias Voltage (V)	Hardness (GPa)														
0	13														
200	16														
400	14														
600	11														
800	8														
1000	6														



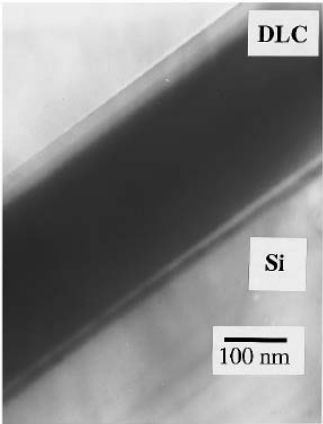
'399 Patent	U.S. Patent No. 5,237,967 ("967 Patent")																
	hydrogenated carbon films at the piston-cylinder interface, and on swash plates used in compressors. (967 patent at 7:43-8:9).																
an interface opposite said surface with a thickness direction extending through said thin film from said interface to said surface, and	<p>More particularly, the invention relates to a component having a hard, wear resistant coating of an amorphous hydrogenated carbon film formed thereupon. (967 patent at 1:9-12).</p> <p>The present invention discloses a powertrain component, such as a valve lifter, or journal or engine bearing for use in an internal combustion engine and a method for applying a hard, wear resistant film which firmly adheres to the component. The present invention also discloses a powertrain component with an amorphous hydrogenated carbon film which significantly reduces friction and wear. Also disclosed is an interlayer system for improving adherence and ability to withstand mechanical stresses. (967 patent at 2:29-38).</p> <p>Accordingly, an object of the present invention is to provide a powertrain component such as a valve lifter for use in an internal combustion engine and a method for applying a hard, wear resistant film which firmly adheres to the component. In such an environment, an amorphous, hydrogenated carbon film is formed thereupon to impart the characteristics of low friction and wear resistance. (967 patent at 2:63-3:2).</p> <div data-bbox="609 1339 1421 1701">  <table border="1"> <caption>Data points estimated from Figure 4A</caption> <thead> <tr> <th>Bias Voltage (V)</th> <th>Hx</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>0.58</td> </tr> <tr> <td>100</td> <td>0.48</td> </tr> <tr> <td>200</td> <td>0.45</td> </tr> <tr> <td>400</td> <td>0.40</td> </tr> <tr> <td>600</td> <td>0.38</td> </tr> <tr> <td>800</td> <td>0.35</td> </tr> <tr> <td>1000</td> <td>0.33</td> </tr> </tbody> </table> </div> <p>(967 patent at Figure 4A).</p>	Bias Voltage (V)	Hx	0	0.58	100	0.48	200	0.45	400	0.40	600	0.38	800	0.35	1000	0.33
Bias Voltage (V)	Hx																
0	0.58																
100	0.48																
200	0.45																
400	0.40																
600	0.38																
800	0.35																
1000	0.33																

'399 Patent	U.S. Patent No. 5,237,967 ("967 Patent")														
	<div data-bbox="581 283 1393 724" data-label="Figure"> <table border="1"> <caption>Data points for FIG. 4B</caption> <thead> <tr> <th>Bias Voltage (V)</th> <th>Hardness (GPa)</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>13</td> </tr> <tr> <td>200</td> <td>16</td> </tr> <tr> <td>400</td> <td>14</td> </tr> <tr> <td>600</td> <td>11</td> </tr> <tr> <td>800</td> <td>8</td> </tr> <tr> <td>1000</td> <td>6</td> </tr> </tbody> </table> </div> <p data-bbox="565 730 906 762">('967 patent at Figure 4B).</p> <p data-bbox="565 804 1442 1308">The mechanical properties of amorphous hydrogenated carbon films, e.g. hardness, elastic modulus, Poisson's ratio, etc. depend on the bias voltage, in addition to the type of hydrocarbon gas used during deposition. The hardness of the films deposited at different bias voltages is shown in FIG. 4B. Hardness reaches a peak, about 16 GPa--as measured by nanoindentation techniques--for hydrogenated carbon films deposited at 200-250 rms bias voltage. Such hardness values are substantially equivalent to 30 GPa when measured by more conventional methods, such as the Vickers test. Hardness decreases monotonically at higher bias voltages. The high hardness of hydrogenated carbon films probably arises from an over-constrained extended network in which small graphitic clusters are captured. The durability of hydrogenated carbon films is optimal at bias voltages ranging from 200 v to 800 v rms.</p> <p data-bbox="565 1350 1442 1707">As noted earlier, hydrogenated carbon films deposited by CVD typically contain large compressive stresses which may sometimes cause buckling of the film. The compressive stress exerted by the film is illustrated in FIG. 4C. The stress is small for polymer-like films, increases to a maximum near 50 v, then decreases monotonically and almost vanishes at 1000 v. As with observations noted earlier, without wishing to be bound by any particular theory, it appears that the decrease in stress may be related to reduced hydrogen content and a transition from an amorphous to a graphite-like morphology with increasing bias voltage.</p> <p data-bbox="565 1749 1442 1892">The disclosed films may be usefully applied to various components, such as engine and journal bearings, besides a valve stem and a valve guide. Other applications include the use of hydrogenated carbon films at the piston-cylinder interface, and on</p>	Bias Voltage (V)	Hardness (GPa)	0	13	200	16	400	14	600	11	800	8	1000	6
Bias Voltage (V)	Hardness (GPa)														
0	13														
200	16														
400	14														
600	11														
800	8														
1000	6														

'399 Patent	U.S. Patent No. 5,237,967 ("967 Patent")
	swash plates used in compressors. (967 patent at 7:43-8:9).
<p>having a graded carbon composition in which a ratio of <math>sp^2</math> to <math>sp^3</math> carbon-carbon bonding in said thin film decreases in said thickness direction from said interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<div data-bbox="609 388 1421 745"> <p>FIG. 4A</p> </div> <p>(967 patent at Figure 4A).</p> <div data-bbox="576 829 1388 1270"> <p>FIG. 4B</p> </div> <p>(967 patent at Figure 4B).</p> <p>As illustrated in FIG. 4A, the composition and morphology of hydrogenated carbon films depends on the negative bias voltage applied (and on the type of gas used as the carbon source). The disclosed films are deposited from methane, although (as noted above) other carbon sources may be used. If deposited at low bias voltages, the films are characteristically organic, or polymer-like. They tend to flow under stress. In such films, the hydrogen content may approach 60 atomic percent and the C-C bonding is predominantly <math>sp^3</math>. As the bias voltage increases, the hydrogen content of the film decreases. This is probably because the increasing bombardment of the films during growth removes weakly bonded hydrogen. In turn, this phenomenon leads to increased C-C bonding.</p> <p>Between 200 v and 800 v rms bias (corresponding to ion kinetic</p>

'399 Patent	U.S. Patent No. 5,237,967 ("967 Patent")
	<p>energy in the range of 50 to 200 electron volts), the reduced hydrogen content and the high <math>sp^3/sp^2</math> ratio produce the desired hydrogenated carbon structure. Above 800 v rms, the low hydrogen content and the greater degree of <math>sp^2</math> bonding produce a graphite-like film. (967 patent at 7:21-42).</p> <p>Hydrogenated carbon films are of interest because of their attributes of high hardness and wear resistance. Such films consist of isolated <math>sp^2</math> carboncarbon (C-C) bonded (graphitic) clusters, the size of which is no larger than 30-40 Angstroms. These clusters may in turn be linked by <math>sp^3</math> C-C bonds to form a rigid three dimensional structure. The film imparts the characteristics of low friction and wear resistance to the component. (967 patent at 5:54-62).</p> <p>Depending upon the conditions, hydrogenated carbon films may contain large amounts (20-60 atomic percent) of hydrogen. The amount of hydrogen incorporated in the film and the preparation conditions strongly influence the properties of the resulting coating. Optimum results occur in the 35-50 atomic percent range. Hydrogen content of the films also determines to a great extent the ratio between the carbon atoms in the different <math>sp^2</math>, <math>sp^3</math>, and even <math>sp^1</math> coordinations. (967 patent at 6:1-9).</p>

'399 Patent	Pharr et al., <i>Hardness, elastic modules, and structure of very hard carbon films produced by cathodic-arc deposition with substrate pulse biasing</i> , Appl. Phys. Lett. 68 (6) (Feb. 1996)																				
Claim 1																					
A hard carbon thin film arrangement comprising	<p>Pharr 1996 APL was published in February 1996, more than one year before the U.S. filing date of the '399 patent.</p> <p>Elements below show a hard carbon thin film.</p>																				
a hard carbon thin film having a surface and	<p>Hardness, elastic modulus, and structure of very hard carbon films produced by cathodic-arc deposition with substrate pulse biasing (Pharr 1996 APL at p. 779)</p> <p>Amorphous carbon has been deposited from a cathodic arc by various groups.<sup>2-8</sup> Hardness values ranging from 26 GPa to over 60 GPa have been measured by nanoindentation methods. The difficulties of deriving hardness values for such hard, thin films on softer substrates are well recognized.<sup>9</sup> Nevertheless, the high values reported suggest that a-C with very high hardness can be achieved by cathodic-arc deposition. (Pharr 1996 APL at p. 779)</p> <p>The key to producing high hardness in amorphous carbon films appears to be in promoting high sp<sup>3</sup> bond content through careful control of the energy of incident ions during deposition. (Pharr 1996 APL at p. 779)</p> <p>TABLE I. EELS results.</p> <table><tr><th>Bias voltage (V)</th><th>Valence plasmon (eV)</th><th>Mass density (g/ cm<sup>3</sup>)</th><th>sp<sup>3</sup> content (%)</th></tr><tr><td>no bias</td><td>29.8</td><td>2.91</td><td>81</td></tr><tr><td>-100</td><td>30.3</td><td>3.00</td><td>85</td></tr><tr><td>-500</td><td>25.8</td><td>2.18</td><td>47</td></tr><tr><td>-2000</td><td>25.6</td><td>2.14</td><td>39</td></tr></table> <p>(Pharr 1996 APL at p. 780)</p> <p>The EELS results are summarized in Table I. The sp<sup>3</sup> content and mass density are greatest for the film deposited at - 100 V, equivalent to an incident ion energy of 120 eV. (Pharr 1996 APL at p. 780)</p>	Bias voltage (V)	Valence plasmon (eV)	Mass density (g/ cm <sup>3</sup> )	sp <sup>3</sup> content (%)	no bias	29.8	2.91	81	-100	30.3	3.00	85	-500	25.8	2.18	47	-2000	25.6	2.14	39
Bias voltage (V)	Valence plasmon (eV)	Mass density (g/ cm <sup>3</sup> )	sp <sup>3</sup> content (%)																		
no bias	29.8	2.91	81																		
-100	30.3	3.00	85																		
-500	25.8	2.18	47																		
-2000	25.6	2.14	39																		
an interface opposite said surface with a thickness direction extending through said thin film from	<p>The films were produced using a two-step process in which a thin layer, approximately 5 nm, was first deposited at the relatively high substrate bias of - 2000 V followed by growth of the majority of the film at - 100 V. The broad interfacial layer produced in this way serves to improve film adhesion and reduce stress at the interface.</p>																				

'399 Patent	Pharr et al., <i>Hardness, elastic modules, and structure of very hard carbon films produced by cathodic-arc deposition with substrate pulse biasing</i> , <i>Appl. Phys. Lett.</i> <b>68</b> (6) (Feb. 1996)
said interface to said surface, and	<p>(Pharr 1996 APL at p. 780)</p>  <p>FIG. 3. A bright field TEM image showing a cathodic-arc film in cross section.</p> <p>(Pharr 1996 APL at p. 781)</p> <p>The film has both surface and interface structure. At the surface, a distinctly lighter layer, on the order of 20 nm thick, is observed in the bright field image. The contrast from this layer is consistent with a lower density material and thus what would probably be a softer form of carbon.</p> <p>(Pharr 1996 APL at p. 781)</p> <p>The structure of the cathodic-arc films was examined in cross section by transmission electron microscopy. A bright field image of a film approximately 300 nm thick is given in Fig. 3...Two distinct layers are observed between the bulk of the film and the silicon substrate, each approximately 10 nm thick. Immediately adjacent to the silicon substrate is a dark layer corresponding to a Si-C reaction layer. This layer is produced by implantation of carbon into the substrate during the - 2000 V high bias applied during the initial portion of the deposition process. Between the reaction layer and the bulk of the film lies a lighter phase which is consistent with lower density carbon codeposited during the high bias deposition.</p> <p>(Pharr 1996 APL at p. 781)</p>
having a graded carbon composition in which a ratio of $sp^2$ to $sp^3$ carbon-carbon bonding in said thin film decreases in said	<p>The films were produced using a two-step process in which a thin layer, approximately 5 nm, was first deposited at the relatively high substrate bias of - 2000 V followed by growth of the majority of the film at - 100 V. The broad interfacial layer produced in this way serves to improve film adhesion and reduce stress at the interface.</p> <p>(Pharr 1996 APL at p. 780)</p>

'399 Patent	Pharr et al., <i>Hardness, elastic modules, and structure of very hard carbon films produced by cathodic-arc deposition with substrate pulse biasing</i> , Appl. Phys. Lett. 68 (6) (Feb. 1996)
<p>thickness direction from said interface to a minimum at an internal location of said thin film between said interface and said surface, and increases from said minimum at said internal location toward said surface of said thin film.</p>	<div data-bbox="638 331 958 753" data-label="Image"> <p>The image is a bright field transmission electron micrograph (TEM) showing a cross-section of a cathodic-arc film. It features a dark, layered structure on a lighter substrate. Labels 'DLC' and 'Si' are present, along with a 100 nm scale bar.</p> </div> <p data-bbox="527 779 1070 821">FIG. 3. A bright field TEM image showing a cathodic-arc film in cross section.</p> <p data-bbox="500 823 852 856">(Pharr 1996 APL at p. 781)</p> <p data-bbox="500 896 1430 1073">The film has both surface and interface structure. At the surface, a distinctly lighter layer, on the order of 20 nm thick, is observed in the bright field image. The contrast from this layer is consistent with a lower density material and thus what would probably be a softer form of carbon.</p> <p data-bbox="500 1077 852 1110">(Pharr 1996 APL at p. 781)</p> <p data-bbox="500 1150 1430 1549">The structure of the cathodic-arc films was examined in cross section by transmission electron microscopy. A bright field image of a film approximately 300 nm thick is given in Fig. 3...Two distinct layers are observed between the bulk of the film and the silicon substrate, each approximately 10 nm thick. Immediately adjacent to the silicon substrate is a dark layer corresponding to a Si-C reaction layer. This layer is produced by implantation of carbon into the substrate during the - 2000 V high bias applied during the initial portion of the deposition process. Between the reaction layer and the bulk of the film lies a lighter phase which is consistent with lower density carbon codeposited during the high bias deposition.</p> <p data-bbox="500 1554 852 1587">(Pharr 1996 APL at p. 781)</p>